



Pyrolysis of switchgrass (*Panicum virgatum* L.) at low temperatures in N₂ and CO₂ environments; a study on chemical composition of chars extracts and bio-oils

Guillaume Pilon, Jean-Michel Lavoie*

Department of Chemical Engineering and Biotechnological Engineering, Université de Sherbrooke, Sherbrooke, Québec J1K 2R1, Canada

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ABSTRACT

With the increasing value addition applications of biomass pyrolysis char such as a soil amendment or feedstock for subsequent thermochemical conversions, chemical composition of char extracts becomes a necessity. Along this study, switchgrass (*Panicum virgatum* L.) was pyrolyzed using two distinct gas vectors, N₂ vs. CO₂, at 300, 400 and 500 °C for 2.5 min in a 25 g/batch fixed bed reactor using a 55 °C/min preheating stage temperature ramp. Chars were extracted with dichloromethane using Soxhlet, and these mixtures, in common with pyrolytic liquids were analyzed by GC–MS. With respect to temperature, the process performed at 500 °C resulted in a significantly lesser amount of char extracts as compared to the ones produced at 300 and 400 °C respectively. Differences were observed with respect to gas environments at the 3 operating temperatures. Among the differences, the pyrolysis performed at 300 °C under CO₂ lead to higher char extracts content compared to N₂ environment (9 vs. 6 mg/g char). Chars obtained at 300 °C–CO₂ had a significantly lower calorific value compared to those from 300 °C–N₂ (22.2 vs. 24.5 MJ/kg respectively). At 400 °C, furfural was only found in char extracts from N₂ gas inflow environment, while in bio-oil, it was also found at significantly higher relative content under N₂ vs. CO₂. The char extracts as well as condensable chemical compounds have demonstrated predominant levels of phenols, cyclopentanones derivatives and furan-derived compounds.

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1. Introduction

Pyrolysis of lignocellulosic biomass is a process by which the feedstock macromolecular compounds are fragmented to smaller molecules by the effect of heat within anoxic or almost anoxic environment. From the three main pyrolysis products, char, gases and liquids, the latter is the fraction that has been characterized more thoroughly due to its multiple possible applications, the variety of compounds it contains as well as for its energy density. The solid residue generated after volatiles loss, the char, is also considered due to the numerous potential applications it proposes such as an improved feedstock for combustion or gasification. It also generates an increased attention as a precursor of activated carbon and as a soil amendment, either for CO₂ sequestration, as a crop growth enhancer or for adsorption of organic and inorganic compounds for environmental purposes (e.g.: N-fertilizer leaching control) [1,2]. Char, with respect to reacting conditions, to biomass type, as well as pre- and post-treatments, may vary chemically and physically [3]. Very few analyses explored the chemical composition of char extracts synergistically with the condensable gases portion. In accordance to Krull et al. [4], the solvent-extractable components

from char have rarely been investigated and could provide valuable insight along char application as a soil amendment; especially in terms of char–soil and/or char–plant interactions studies, without making abstraction of the environmental point of view. Char chemical composition may also be of interest for further downstream processes where it would serve as a feedstock.

Hale et al. [5] recently published one of the few studies about PAHs and dioxins presence in char extracts. They analyzed mostly slow pyrolysis chars from several biomass sources, reactor types and production methods (temperatures from 250 to 900 °C) and quantified the total PAH presences in those chars. They concluded that the total as well as the bioavailable contents of PAHs and dioxins monitored in their slow pyrolysis chars were below environmental levels (threatening levels) for soil application. However, the authors specified that their results should not be extended any more than for slow pyrolysis chars and especially in their studied conditions.

As well, the use of CO₂ as an inflow gas environment in low temperatures pyrolysis conditions has not been thoroughly investigated in open literature. Pyrolysis or other thermochemical conversion processes in general are showing genuine interest for recycling flue gases and residual CO₂, although, most of the reported experiments used carbon dioxide at higher temperatures (above 600 °C). Despite the fact that CO₂ is generally considered to be inert at low temperatures [6], interesting behaviors may be

* Corresponding author. Tel.: +1 819 821 8000; fax: +1 819 821 7955.

E-mail address: jean-michel.lavoie2@usherbrooke.ca (J.-M. Lavoie).

observed at low pyrolysis temperatures of 300, 400 and 500 °C [7]. Potential interaction of CO₂ with chemical functions of the biomass appeared to exist based on differences noted in CO₂ vs. N₂ atmosphere among the yields and characteristics of the 3 main products (chars, liquids and non-condensable gases). Usually unfavorable at such temperature, the mineral content of the biomass' ashes might have promoted interactions such as fixing CO₂ (COO + H) as a carboxylic acid function.

Similar possible reaction was observed through results of Zhang et al. [8] and Jindarom et al. [9] who pyrolyzed corncobs at 550 °C and sewage sludge at 350–650 °C respectively, both within a CO₂ environment. They both analyzed their bio-oils and observed an increase of compounds containing carboxylic acid functions while operating in CO₂ in comparison to N₂ environment. In addition, Zhang et al. [8] observed an increase in acid content and overall lesser amounts of phenol derivatives and sugars. On the other hand, the phenol concentration (C₆H₆O) of their bio-oils reached a higher content following pyrolysis in a CO₂ environment. In general there was also a correlation with the lesser amount of methoxy function when using CO₂, which could be consistent with the overall higher concentrations of acetic acid, leading to the assumption that CO₂ has been fixed as a carboxylic acid function. The authors also compared calorific values of condensable products and they observed an increase from 17.8 MJ/kg with N₂ to 20.2 MJ/kg in CO₂ environment. Jindarom et al. [9] generally observed more oxygenated compounds in CO₂ atmosphere, a reduction in aliphatic content and an enhancement in carboxylics and ketones formation.

Switchgrass (*Panicum virgatum*) is a potential energy crop, native from North America, which represents an interesting feedstock for pyrolysis. Work reported on pyrolysis of this feedstock presented bio-oils composition in standard inert atmosphere (i.e. N₂). Generally bio-oils showed contents rich in acetic acid, furfural, acetol, levoglucosan, guaiacol and phenol; contents that approach typical wood bio-oils values [10–13].

This work presents the chemical analysis of the char extracts as well as condensable gases (bio-oils) from the pyrolysis of switchgrass (*P. virgatum*) at 300, 400 and 500 °C within N₂ and CO₂ environments. Char extracts composition linked to the bio-oils compositions in addition of using CO₂ as an inflow gas environment in low temperatures pyrolysis conditions are rather scarce in literature for those specific conditions as well as for pyrolysis in general.

2. Materials and methods

2.1. Experimental setup

The experimental setup and the process have been previously described in details in the study of Pilon and Lavoie [7] and no modifications were made for this experiment. About 25 g of switchgrass at an initial moisture content level of 4–9% were pyrolyzed per test. During the process, the feedstock is first inserted in the sealed reactor and heated using nitrogen or carbon dioxide as heat vector gases (0.5 L/s). Heating is started at 55 °C/min, up to the reactor's desired operating temperature. Operating temperatures (300, 400 and 500 °C) were maintained for 2.5 min after what the vector gas' inflow was stopped and the reactor was cooled down to room temperature. Each studied pyrolysis reaction condition was conducted in triplicates. Statistical comparisons among the results were done with one factorial ANOVA; mostly looking at the gas environment effect per specific operating temperature. Condensable products were collected along a series of 4 chilled condensers (glass tubes in water and ice) installed right after the reactor. All along the report, in order to alleviate the text, samples abbreviations are given as follow: {(C or L)(3, 4 or 5)(N or C)} standing for {(char

or liquid bio-oil), (300, 400 or 500 °C), and (N₂ or CO₂)} (ex.: C3N corresponds to char produced at 300 °C, in a N₂ environment).

2.2. Solid material extraction and bio-oil preparation

For each extraction, 3 g of biomass char (~90% 10–200 mesh particle size) was placed in a cellulose cartridge (25 mm ID × 90 mm) and extracted with 150 mL of methylene chloride. Extractions were performed for 8 h, after which the solvent and extracts were filtered to remove any char particles before being transferred to a round-bottom flask for concentration using a rotary evaporator. Each concentration was done at 40–45 °C under a vacuum of 50 kPa relative to ambient pressure. Concentration was performed until complete solvent evaporation. The remaining extracts were collected using 1–2 mL of dichloromethane in order to have a sufficiently concentrated extract for GC–MS analysis.

Condensable products were collected from each of the condensing tubes and connecting lines. The content was collected using acetone after which the solution was filtered through glass frit funnel to remove any particles. Prior to analysis, acetone was completely removed by rotary evaporator (at 65 °C and under a vacuum of 50 kPa relative to ambient pressure). After concentration, the bio-oils samples (homogeneous) were mixed with dichloromethane for further GC–MS analysis. The identification of char extracts and condensable products GC–MS have been performed with the NIST mass spectra database (for ≥85% correlation spectrum identifications) while the gas effect comparison per specific temperature was performed from relative compounds content (area based), calculated from the peak area of the total ion chromatogram.

2.3. Products characterization and GC–MS analysis

The gas chromatograph utilized is an Agilent 6890N network GC system with 5973 network mass selective detector. The column was a DB-5ms MSD (30 m × 0.25 mm) (#122-4532). Each sample was analyzed in a splitless mode, no pulse, at 2 µl/injection and with 2 min solvent delay. Gas chromatography and mass spectroscopy were performed using temperatures of 250 °C (inlet) and of 250 °C (detector) (MS: 200 V, EI: 70 eV, mass range: 10–400 g/mol). The oven's temperature program started at 60 °C for 3 min, followed by a temperature increase (4 °C/min) up to 310 °C which was maintained for 1 min. Methods used for elemental composition, calorific value, Karl Fisher water content, proximate analysis conducted for switchgrass, chars and/or condensable products are presented in Pilon and Lavoie [7].

3. Results and discussions

3.1. Char extracts and bio-oils chemical composition

Looking at char extracts in general, it can be observed that char extracted amounts varied with respect to temperature and gas environment (Fig. 1). With respect to temperature, 500 °C conditions resulted in significantly lesser amount of char extracts compared to the ones produced at 300 and 400 °C respectively. This result is in agreement with higher feedstock conversion (lower char and higher gases yields) resulting from the higher temperature level and to the lower volatile content in chars produced at 500 °C (Table 1). With respect to gas environment, as presented in Table 1 and discussed in further details in Pilon and Lavoie [7], at 300 °C-CO₂, char had higher volatiles content ($P=0.1$) and the bio-oil yield was significantly lower ($P<0.002$) compared to the 300 °C-N₂ conditions. Char extracts results obtained for 300 °C chars are in agreement with these results since the extracted amount (on a char basis) is higher under CO₂ atmosphere. The

Table 1
Physicochemical characteristics of raw switchgrass, chars and bio-oils.

Conditions		Yields ^c		Raw Switchgrass and Chars										Bio-oils		
HHT [°C]	Gas Env.	Char [%] ^a	Oil [%] ^a	Gas [%] ^{a,b}	C [%] ^d	H [%] ^d	O [%] ^d	N [%] ^d	H/C ^d	O/C ^d	Ash [%] ^{c,d}	Volatiles [%] ^{c,d}	FC [%] ^{c,d}	HHV [MJ/kg] ^d	HHV [MJ/kg]	Water [%] ^c
Switchgrass		n.a.	n.a.	n.a.	47.1 ± 0.5	5.4 ± 0.0	42.7 ± 0.8	0.6 ± 0.0	1.4	0.7	3.7 ± 0.2	81.0 ± 0.2	15.3 ± 0.2	20.7 ± 1.1	n.a.	n.a.
300	N ₂	54.4 ± 2.2	24.6 ± 0.6	21.0 ± 2.4	54.7 ± 0.7	4.7 ± 0.1	34.2 ± 2.4	0.7 ± 0.1	1.0	0.5	7.3 ± 1.0	57.1 ± 0.6	35.6 ± 1.2	24.5 ± 1.1	15.4 ± 2.0	26.6 ± 5.3
300	CO ₂	59.2 ± 4.1	18.0 ± 1.5	22.7 ± 4.7	53.7 ± 0.8	4.9 ± 0.2	34.6 ± 1.2	0.7 ± 0.1	1.1	0.5	6.3 ± 0.5	61.0 ± 3.9	32.8 ± 3.5	22.2 ± 0.7	15.7 ± 1.1	23.5 ± 12.9
400	N ₂	36.7 ± 2.9	35.6 ± 3.3	27.7 ± 3.4	61.1 ± 2.5	3.6 ± 0.4	22.8 ± 2.8	0.8 ± 0.0	0.7	0.3	10.8 ± 0.7	35.8 ± 2.8	53.5 ± 3.4	26.6 ± 2.0	15.8 ± 1.6	25.5 ± 5.3
400	CO ₂	35.9 ± 1.6	33.7 ± 1.4	30.4 ± 2.2	61.5 ± 0.1	3.7 ± 0.3	21.1 ± 1.9	0.9 ± 0.1	0.7	0.3	11.5 ± 0.3	36.5 ± 2.1	52.0 ± 1.9	25.8 ± 1.6	15.4 ± 1.1	27.6 ± 3.6
500	N ₂	28.2 ± 0.7	37.7 ± 0.7	34.1 ± 0.7	63.8 ± 1.3	2.5 ± 0.1	20.0 ± 0.5	0.8 ± 0.1	0.5	0.2	13.5 ± 0.6	28.3 ± 1.9	58.3 ± 1.7	26.7 ± 1.2	14.0 ± 1.1	39.0 ± 2.2
500	CO ₂	28.1 ± 0.8	36.0 ± 0.6	35.9 ± 1.1	64.4 ± 2.0	2.5 ± 0.0	19.0 ± 0.5	0.7 ± 0.1	0.5	0.2	11.5 ± 0.7	24.8 ± 3.4	63.7 ± 3.1	28.3 ± 1.6	15.6 ± 1.4	36.7 ± 2.6

Legend: HHT: Higher Heating Temperature; Env.: Environment; FC: Fixed carbon; HHV: Higher Heating Value.

^a Expressed on a raw biomass (dry basis).

^b Obtained by difference.

^c Source: [7].

^d Dry basis. "±" corresponds to std. dev. (for n = 3).

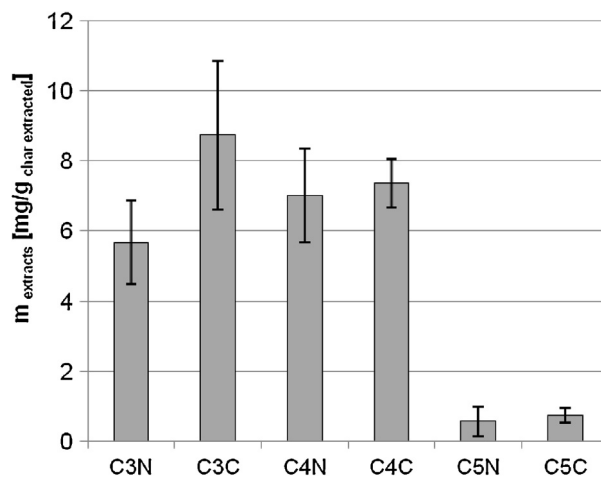


Fig. 1. Mass of extracts generated by the char Soxhlet extractions using dichloromethane. Error bars correspond to standard deviation.

char extracts may correspond to the volatiles that condensed on the char matrix during their expulsion.

Char extracts contain a wide variety of compounds with several types of functionalities. These compounds may have been formed along decomposition and recombination reactions and possibly condensed back in char along the expulsion process [14]. Due to a relatively short residence time of 2.5 min within the studied conditions (compared to slow pyrolysis) this might have favored higher condensed volatiles content (tar) on the char itself instead of enhancing their release [5]. The actual conditions are most representative of a medium pyrolysis due to the heating rate level and residence time [3,15,16].

Among the identifications, only a few different types of alkanes were observed in C3N (all with a low relative content) and none of them were present within C3C (Table 2). A reason explaining the different types of alkanes found at 300 °C may be in part related to the decomposition of the extractives, starting around 200 °C up to 600 °C [17]. Extractives (and most specifically long chain fatty acids found in switchgrass extractives [18]) are known to decarboxylate at such temperature and possibly to pass through cracking reactions, which could explain the occurrence of long alkane chains [9,19,20]. The fact that the C3C samples did not contain any of these long alkane chains shows that CO₂ has an effect on the extracts at that specific temperature. This behavior might be explained by the extraction of alkanes in this condition (C3C) that would be inhibited by a new link resulting from CO₂ environment. Biomass feedstock is known to decarboxylate at torrefaction temperature [21], however, CO₂ environment may reduce the decarboxylation and even enhance the carboxylation from CO₂ reacting with the alkane molecular sections leading to more acidic compounds. These new acid compounds expected to be more polar, may become less prone to be leached by the solvent. It has to be noted that at 500 °C, despite the fact a high relative content of alkanes was found in the char extracts (Fig. 2), the amount of alkane extracts (on a char basis; related to Fig. 1) would be similar to the ones produced at lower temperatures. The relative contents would, however, be higher under CO₂ atmosphere (vs. N₂) for 500 °C as well as for 400 °C results (respectively), which is the inverse as the behavior observed under 300 °C. Differences observed among identified alkanes components with respect to gas environment for 400 and 500 °C respectively are, however, not statistically significant.

Compounds identified in char extracts are mostly phenol derivatives (Table 2). Phenols may be found in raw switchgrass, tightly bound within lignin structure or as part of other extractable phenolics [22]. A higher relative content of phenol derivatives was

Table 2GC–MS compounds identifications of chars DCM extractions and bio-oil (Contents obtained from GC peak area, for $n = 3$ and for *, $n = 2$).

Compounds	CAS #	Char extracts by DCM						Condensable products					
		C3N	C3C*	C4N	C4C	C5N	C5C	L3N	L3C	L4N	L4C*	L5N	L5C
Alkanes and cycloalkanes													
Undecane	001120-21-4						0.81						
Dodecane	000112-40-3					0.32	4.35						
Tridecane	000629-50-5	0.06		0.23	0.23	3.46	9.51						
Tetradecane	000629-59-4	0.22		0.11	0.24	2.19	1.74						
Pentadecane	000629-62-9	0.49		0.17	0.34	2.53	4.80						
Hexadecane	000544-76-3	0.12		0.14	0.18	1.43	1.13						
Heptadecane	000629-78-7	0.17		0.10	0.21	2.43	0.18						
Octadecane	000593-45-3	0.12		0.13	0.13	0.56							
Nonadecane	000629-92-5			0.13	0.33		0.46						
Eicosane	000112-95-8	0.09		0.04	0.08								
Heneicosane	000629-94-7			0.06	0.13								
Cyclododecane	000294-62-2			0.13	0.08								
Total (relative content):	%	1.27	0.00	1.24	1.94	12.92	22.97	0.00	0.00	0.00	0.00	0.00	0.00
Phenol derivatives													
Phenol	000108-95-2	4.82	3.82	4.09	5.78		1.42	1.66	1.87	2.27	2.16	3.64	3.60
Phenol, 2-methyl-	000095-48-7	2.19		0.99	1.95	2.22	4.89			1.12	0.58	1.29	1.45
Phenol, 3-methyl-	000108-39-4	0.27				3.09	1.76	0.09					
Phenol, 4-methyl-	000106-44-5	3.70	0.41	2.29	4.93	0.39	5.93	0.11	0.17	0.82	0.63	2.14	2.48
Phenol, 2-ethyl-	000090-00-6	0.63	1.08		0.23	0.43							
Phenol, 4-ethyl-	000123-07-9	4.28	1.89	3.40	3.66	0.49		0.56	0.70	0.75	0.76	0.71	0.81
Phenol, 2,3-dimethyl-	000526-75-0			0.10	0.70	0.64							
Phenol, 2,4-dimethyl-	000105-67-9			0.18	0.79	0.64	2.51					0.08	0.11
Phenol, 2,5-dimethyl-	000095-87-4					0.42	2.32						
Phenol, 3,4-dimethyl-	000095-65-8	0.34			0.34		0.61						
Phenol, 3,5-dimethyl-	000108-68-9	1.89		0.08	0.17	4.08	3.64						0.09
Phenol, 2-methoxy-	000090-05-1	8.43	8.50	5.89	11.83			4.05	4.32	5.27	4.48	5.41	5.56
2-Methoxy-6-methylphenol	002896-67-5	0.69			1.32								
Phenol, 2-methoxy-4-methyl-	000093-51-6	5.36	3.43	6.44	8.33			1.43	1.30	2.50	2.18	2.59	2.64
Phenol, 2-ethyl-6-methyl-	001687-64-5			0.08	0.05								
Phenol, 3-ethyl-5-methyl-	000698-71-5	0.25			0.27								
Phenol, 4-ethyl-2-methoxy-	002785-89-9	7.71	5.63	6.21	5.79			1.37	1.49	1.87	1.74	1.82	1.92
Phenol, 2,6-dimethoxy-	000091-10-1	1.91	2.55	3.05	1.71			0.64	0.71	1.01	1.03	0.94	1.02
2-Methoxy-4-vinylphenol	007786-61-0	1.63	2.05	0.59				3.29	3.84	2.82	3.51	2.70	2.84
Phenol, 2-methoxy-3-(2-propenyl)-	001941-12-4								0.09	0.09	0.13		
Phenol, 2-methoxy-4-propyl-	002785-87-7	0.18	0.34	1.02	0.68			0.02		0.18	0.08		
3-Allyl-6-methoxyphenol	000501-19-9				0.06					0.08	0.14		
Eugenol (or 2-methoxy-4-(2-propenyl)phenol)	000097-53-0		0.64					0.05					
Phenol, 2-methoxy-4-(1-propenyl)-,(E)-	005932-68-3	0.61	0.75	0.70	0.16			0.58	0.63	0.70	0.73	0.57	0.56
Phenol, 2-methoxy-3-methyl-	018102-31-3			0.44	0.81					0.06			
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	006627-88-9							0.03		0.09	0.13		
Vanillin (or 4-hydroxy-3-methoxybenzaldehyde)	000121-33-5							0.02	0.04	0.02	0.10		
Total (relative content):	%	44.9	31.1	35.6	49.5	12.4	23.1	13.9	15.2	19.6	18.3	21.9	23.1
Ketones													
Acetophenone	000098-86-2			0.09	0.05								

Table 2 (Continued)

2-Pentadecanone, 6,10,14-trimethyl	000502-69-2							0.01	0.03		0.03		
2-Cyclohexen-1-one	000930-68-7			0.06	0.14								
Total (relative content):	%	0.00	0.00	0.15	0.20	0.00	0.00	0.01	0.03	0.00	0.03	0.00	0.00
<i>Cyclopentanone derivatives</i>													
Cyclopentanone	000120-92-3			0.31	1.71								
2-Cyclopenten-1-one	000930-30-3				0.17								
2-Cyclopenten-1-one, 2-methyl-	001120-73-6	0.34		1.44	1.78			0.42	0.37			0.51	0.45
2-Cyclopenten-1-one, 3-methyl-	002758-18-1	0.61		2.50	3.59								
2-Cyclopenten-1-one, 2,3-dimethyl-	001121-05-7	0.84		1.12	2.17				0.11	0.53		0.52	0.52
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	000080-71-7	1.29	1.62	1.85	1.63			1.32	1.40	2.16	2.12	1.86	1.99
2-Cyclopenten-1-one, 3,4-dimethyl-	030434-64-1			0.19	0.18								
2-Cyclopenten-1-one, 2-hydroxy-	010493-98-8							3.94	3.94	4.96	5.97	3.92	2.77
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	021835-01-8		0.10	0.16				0.10	0.25	0.48	0.51		
2-Cyclopenten-1-one, 3-ethyl-	005682-69-9		0.08	0.26	0.27					0.02	0.14		
Total (relative content):	%	3.08	1.80	7.84	11.50	0.00	0.00	5.77	6.07	8.15	8.51	6.80	5.73
<i>Furan derivatives</i>													
2-Furanmethanol	000098-00-0	3.21	6.84	1.91	0.52			4.35	4.98	4.79	5.06	4.92	4.89
2-Furancarboxaldehyde, 5-methyl-	000620-02-0			1.60	1.26			0.59		0.30	0.58	0.51	0.43
Ethanone, 1-(2-furanyl)-	001192-62-7			1.11	1.06								
2(5H)-Furanone, 5-methyl-	000591-11-7									0.11	0.38		
Butyrolactone (or 2(3H)-furanone, dihydro-)	000096-48-0	3.19	6.08	4.17	2.60				0.54				0.40
Furfural	000098-01-1	3.33	3.93	3.86				8.43	7.78	6.59	6.05	7.99	7.26
Total (relative content):	%	9.74	16.84	12.65	5.44	0.00	0.00	13.49	13.30	11.79	12.07	13.42	12.98
<i>Benzofuran derivatives</i>													
Benzofuran	000271-89-6						0.18						
Benzofuran, 7-methyl-	017059-52-8						0.20						
Benzofuran, 2,3-dihydro-	000496-16-2									0.56	1.51	1.28	
Benzofuran, 2-methyl-	004265-25-2			0.41	0.23								
Total (relative content):	%	0.00	0.00	0.41	0.23	0.00	0.38	0.00	0.00	0.56	1.51	1.28	0.00
<i>Ethylbenzene derivatives</i>													
Benzene, 1-ethyl-2-methyl-	000611-14-3						0.28						
Benzene, 1-ethyl-4-methoxy-	001515-95-3			0.17	0.31								
Benzene, 4-ethyl-1,2-dimethoxy-	005888-51-7	0.19		0.10	0.38								
<i>Methoxybenzene derivatives</i>													
Benzene, 1-methoxy-4-methyl-	000104-93-8			0.35	0.53								
Benzene, 1,2-dimethoxy-	000091-16-7			0.08	0.22								
3,4-Dimethoxytoluene	000494-99-5	0.22		0.25	0.43								
<i>Methylbenzene derivatives</i>													
Benzene, 1,3,5-trimethyl-	000108-67-8						0.42						
Benzene, 1,2,3,4-tetramethyl-	000488-23-3						0.18						
<i>Other benzene derivatives</i>													
Bicyclo[4.2.0]octa-1,3,5-triene	000694-87-1			0.12	0.28								
Total (relative content):	%	0.41	0.00	1.07	2.15	0.00	0.88	0.00	0.00	0.00	0.00	0.00	0.00
<i>1H-Indene derivatives</i>													
1H-Inden-1-one, 2,3-dihydro-	000083-33-0	0.76			0.82					0.04	0.05		
1H-Inden-1-one, 2,3-dihydro-3-methyl-	006072-57-7			0.23	0.33								
Total (relative content):	%	0.76	0.00	0.23	1.19	0.00	0.00	0.00	0.00	0.04	0.05	0.00	0.00

Table 2 (Continued)

Compounds	CAS #	Char extracts by DCM						Condensable products					
		C3N	C3C*	C4N	C4C	C5N	C5C	L3N	L3C	L4N	L4C*	L5N	L5C
Naphthalene derivatives													
Naphthalene, 1-ethyl-	001127-76-0					0.35	0.18						
Naphthalene, 1,4-dimethyl-	000571-58-4						0.25						
Naphthalene, 2,3-dimethyl-	000581-40-8					0.43							
Naphthalene	000091-20-3						0.87						
Naphthalene, 2-methyl-	000091-57-6					1.57	2.69						
Naphthalene, 1,7-dimethyl-	000575-37-1					0.20	1.40						
Naphthalene, 1,6,7-trimethyl-	002245-38-7					0.67	0.33						
Naphthalene, 1,8-dimethyl-	000569-41-5						0.19						
Naphthalene, 2,7-dimethyl-	000582-16-1					1.22	2.52						
Naphthalene, 1,6-dimethyl-	000575-43-9					0.72							
Naphthalene, 2,6-dimethyl-	000581-42-0					1.49	2.09						
Total (relative content):	%	0.00	0.00	0.00	0.00	6.65	10.52	0.00	0.00	0.00	0.00	0.00	0.00
Alkenes and cycloalkenes													
5-Tetradecene, (E)-	041446-66-6						0.25						
1-Tridecene	002437-56-1	0.07			0.08	0.35	0.15						
Total (relative content):	%	0.07	0.00	0.00	0.08	0.35	0.40	0.00	0.00	0.00	0.00	0.00	0.00
Carbohydrate derivatives													
1,4:3,6-Dianhydro- α -D-glucopyranose	4451-30-3	1.58	0.72	1.81	1.11	2.66			0.07	0.35	0.42		0.14
2,3-Anhydro-D-mannosan	1000129-98-0			0.15	0.06						0.09		
Total (relative content):	%	1.58	0.72	1.96	1.17	2.66	0.00	0.00	0.07	0.35	0.51	0.00	0.14
Acids													
Propanoic acid	000079-09-4							2.34	1.75	0.28	1.43	0.79	1.39
Hexadecanoic acid, methyl ester	000112-39-0	0.13	0.16	0.13	0.33								
Pentadecanoic acid, 14-methyl-, methyl ester	005129-60-2	0.15	0.16	0.23									
Total (relative content):	%	0.28	0.32	0.36	0.33	0.00	0.00	2.34	1.75	0.28	1.43	0.79	1.39
Alcohol													
1-Hydroxy-2-butanone	005077-67-8	1.22	3.00					3.60	7.64				
Aldehydes													
Cyclopropaneoctanal, 2-octyl-	056196-06-6		0.32										
Ester													
2H-Pyran-2-one, tetrahydro-	000542-28-9	0.22		0.45	0.46								
Others													
Azulene, 4,6,8-trimethyl-	000941-81-1						0.11						
Grand total (relative content):	%	63.5	54.0	62.0	74.2	35.0	58.4	39.1	44.0	40.8	42.4	44.2	43.3

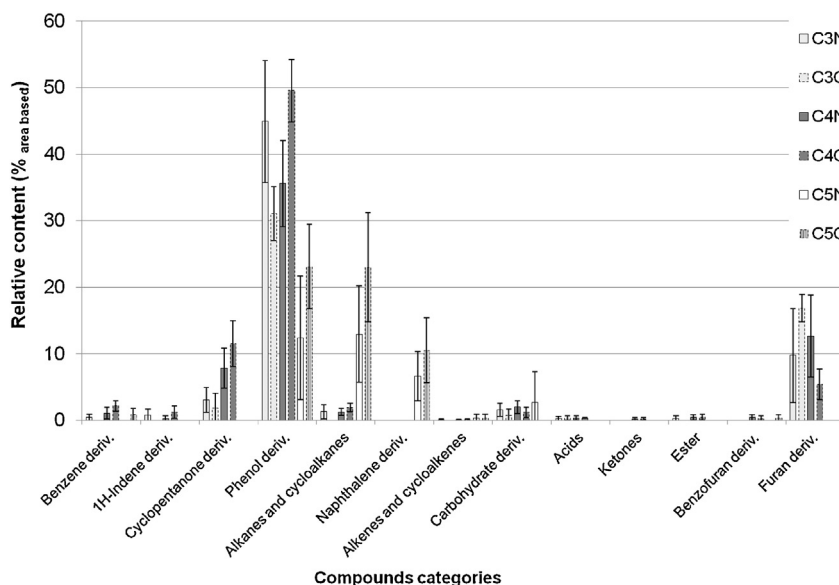


Fig. 2. Relative content of char extracts identified compounds categories. Error bars correspond to standard deviation.

reported in the char extracts at 300 °C in N₂ with regards to the CO₂ environment (45% vs. 31%), however since more char extracts were obtained under CO₂ (Fig. 1), the real content (on a char basis) could show that both gas vectors generated overall comparable amounts of phenolics. On the other hand, results differed at 400 and 500 °C where phenols derivatives appear to be enhanced by CO₂ environment, especially for char extracts (relative contents of 36 and 50% at 400 °C and 12 and 23% at 500 °C for N₂ and CO₂ environments respectively; Table 2). Following that trend, phenol, 4-methylphenol, 2,4-dimethylphenol showed a significant difference with respect to gas environment; all were in char extracts, from 400 °C ($P=0.09$), 500 °C ($P=0.01$) and 500 °C ($P<0.04$) respectively. Results have shown that there is a tendency for phenol derivatives to decrease in char extracts with increasing temperature, mostly at 500 °C, which seems to be consistent with the increasing phenols concentrations in the bio-oils composition with respect to temperature (Table 2, Fig. 2, Fig. 3). The behavior of phenols with respect to temperature is supported with the observations showing that

char extracts decreased and bio-oils yields increased when temperature was increased from 300 to 500 °C (Fig. 1, Table 1). This is also consistent with phenols generally obtained following the thermal degradation of the phenyl unit composing lignin [23] and lignin known to degrade at temperature ranging from 225 up to about 625 °C [24]. It can be noted that phenol, 4-methylphenol and 2-methoxy-4-methylphenol are among the phenol derivatives found in bio-oils that show an increase in relative content with respect to temperature. These results are consistent with literature where phenols have been reported to increase in bio-oils with temperature (up to about 600 °C) and where mostly alkyl phenolics may be found [14]. In bio-oils, with respect to gas environment, the phenol derivatives relative content at 300 °C differs from 13.9% to 15.2% (N₂ and CO₂ respectively); a difference which could be inverted if these phenol yields were transferred on an original biomass basis since bio-oil yield was significantly lower at 300 °C under CO₂ environment (Table 1). Still in char extracts, most of the phenol derivatives containing methoxy group(s) are

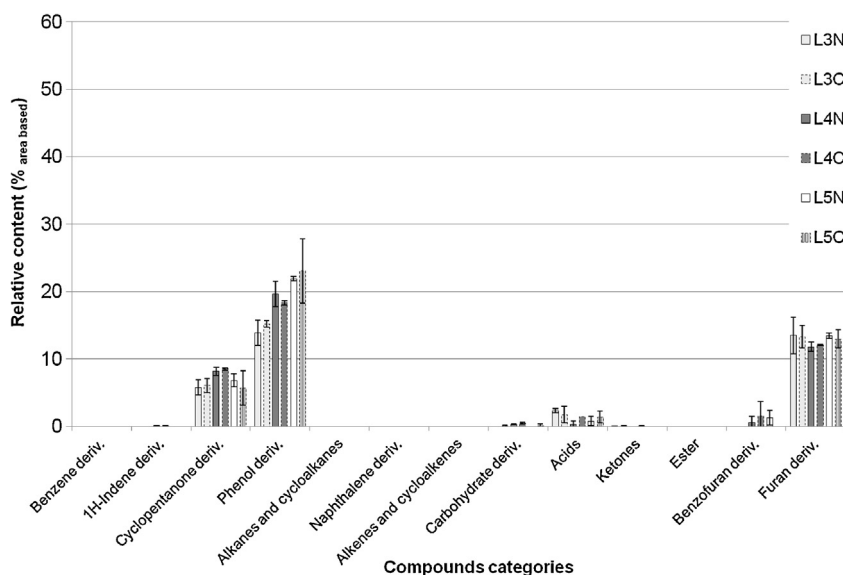


Fig. 3. Relative content of bio-oils identified compounds categories. Error bars correspond to standard deviation.

present only at 300 and 400 °C (Table 2). Among the phenol derivatives products following that behavior, 2-methoxy-phenol (guaiacol), 2-methoxy-4-methyl-phenol (4-methylguaiacol), 2,6-dimethoxyphenol (syringol) and 4-ethyl-2-methoxy-phenol are present in higher concentrations. Loss of methoxy functions from aryl lignin structure were observed to occur with increasing level of severity conditions [25], although this reaction was observed at lower temperature and in an aqueous NaOH mixture, to a certain extent it could be extrapolated to what was observed in our case and for other pyrolysis reactions at 450–500 °C [23]. These results are consistent with the increasing phenol content (C_6H_6O) observed in bio-oils at 500 °C (Table 2) [23].

Among the ketones (including cyclopentanone derivatives), results showed that none could be observed within chars produced at 500 °C which, in this case, could be related to the complete degradation of carbohydrates structures from hemicelluloses or cellulose (Table 2). Ketones are well known to be produced mostly from hemicelluloses and cellulose degradation [26,27]. The loss of carbonyl groups shows to be in agreement with gas yields increase at that temperature (Table 1). Cyclopentanone derivatives are among the major compounds found in bio-oil for every temperature (Table 2, Fig. 3). Cyclopentanone derivatives in char extracts seemed to be affected by the gas environment since an overall lower relative content was obtained with the use of CO_2 compared to N_2 for 300 °C chars (1.80 vs. 3.08% respectively) (Table 2). This difference might be attenuated by the higher extraction yields obtained for the 300 °C- CO_2 chars (i.e.: on a char basis). On the other hand, some specific compounds such as 2-methyl-2-cyclopenten-1-one, 3-methyl-2-cyclopenten-1-one, 2,3-dimethyl-2-cyclopenten-1-one were solely found in char extracts when using N_2 (at 300 °C). Lower percentage of ketones resulting from the CO_2 environment at 300 °C may once again result from the CO_2 that reacted with some of the compounds by carboxylation, increasing their polarity, therefore less prone to being solubilised by dichloromethane. Chars produced at 400 °C also showed a difference with respect to gas environment, (total relative content of 7.8% vs. 11.5% for C4N and C4C respectively) (Table 2). This behavior is consistent with Jindarom et al. [9] who explained the increasing ketones content under CO_2 by the insertion of CO_2 through unsaturated compounds. Among the in bio-oils compounds, the 2-hydroxy-2-cyclopenten-1-one showed a significant difference in that sense; higher content under CO_2 vs. N_2 ($P < 0.07$).

Chars produced at 500 °C also seemed to enhance the release of compounds such as furan derivatives, alcohol, as well as other benzene derivatives (Table 2). Much of these compounds, found at lower temperatures (300 and 400 °C), are not present in the 500 °C char extracts. For all the benzene derivatives that are mostly present at 400 °C, the increment of temperature towards 500 °C might have favored the formation of naphthalene derivatives within char which are mostly found at 500 °C (Table 2). This would be consistent with a known mechanism, where a temperature increase would result in aromatic rings losing their functional groups and eventually recombining into PAHs [28,29]. It is also consistent with the observation previously made by Pilon and Lavoie [30] despite the important fact that the reactor's operation was different (higher heating rate, higher convection, and partial oxidation). Reduction in H/C and O/C ratios observed for the char's production temperature is in agreement with an increase in polyaromatic compounds concentration among char composition (Tables 1 and 2). On the other hand, PAHs concentrations in char were observed by Hales et al. [5] to be at higher levels following low pyrolysis temperatures, while Keiluweit et al. [31] similarly observed their maximum char PAHs concentrations at 400–500 °C; both for slow pyrolysis, at low heating rates and possibly low convection conditions. In both cases, their studies resulted

in several types of higher molecular weight PAHs for temperatures from 300 to 500 °C [5,31] compared to this study, which only lead to low molecular weight naphthalene derivatives. As a result, heating rate, char residence time, gas flow and gas residence time could account for the PAHs formation, which would be an interesting subject for further investigations. In accordance to Hale et al. [5], PAHs have strong sorption on char due to the π - π interaction between the char and the coplanar structure of PAHs themselves, while some of the PAHs might also be trapped within char structure as a result of mechanical occlusion in the char's pore. As a result, more PAHs could possibly be expected due to inadequacy of the dichloromethane to extract all the compounds, which could be more easily extracted by an aromatic solvent as toluene. On a soil amendment point of view, despite the presence of naphthalene derivatives, the quantification of bioavailable PAHs would be of importance since it may differ than the total PAHs available [5]. As for the effect of the gas environment, CO_2 seemed to have enhanced some naphthalene derivatives formation since 1,7-dimethyl-naphthalene and 2,7-dimethyl-naphthalene showed an increase of more than twofold for about the same char extracts content (C5N vs. C5C; Fig. 1) and the compounds category total relative content passing from 6.7 to 10.5% (N_2 vs. CO_2 respectively) (Table 2). No PAH was detected in the condensed liquids.

Among the carbohydrate derivatives found in char extracts, the 1,4:3,6-dianhydro- α -D-glucopyranose was found at higher concentrations at 500 °C- N_2 with regards to any other studied conditions (Table 2). This can simply result from lower char extracts yields at 500 °C (Fig. 1), which would in fact lead to concentration similar to 300 and 400 °C chars (on a char basis). Noteworthy that 1,4:3,6-dianhydro- α -D-glucopyranose saccharide was only observed in C5N, but not in C5C conditions (Table 2). In addition, lower levels of 1,4:3,6-dianhydro- α -D-glucopyranose were also observed at C3C and C4C compared to C3N and C4N respectively. This behavior may signify that once again carboxylation could have occurred, reacting with 1,4:3,6-dianhydro- α -D-glucopyranose or its precursor, adding acidic function(s) $COO + H$ and as a result would have been less prone to solubilisation with dichloromethane. Nonetheless, the lower content of 1,4:3,6-dianhydro- α -D-glucopyranose affected by CO_2 environment could also be in agreement with lower furfural content for the C4C conditions compared to C4N (Table 2). The 1,4:3,6-dianhydro- α -D-glucopyranose has been proposed to precede furfural formation [32]. Furfural was also identified in bio-oils with slightly higher relative content under N_2 for each studied temperature (8.4 vs. 7.8; 6.6 vs. 6.1 and 8.0 vs. 7.3 for L3N vs. L3C; L4N vs. L4C and L5N vs. L5C respectively; significant at 400 °C for $P < 0.065$). Despite the fact furfural was not found at C4C, C5N and C5C, these conditions (and especially 400 °C- CO_2) does not seem to impair furfural formation since this latter is present in bio-oils. The low 1,4:3,6-dianhydro- α -D-glucopyranose content in bio-oils, could be due to a better affinity of this later compound with aqueous bio-oil fraction than with CH_2Cl_2 . Furfural is also considered being an hemicelluloses degradation product where cellulose presence or degradation products would enhance furfural formation [27,32]. The presence of furfural in chars extracts at 300 and 400 °C (Table 2) would then be consistent with hemicelluloses and cellulose transformation known to occur around 225–300 °C and 305–375 °C respectively [33].

It is possible to notice, among GC-MS identifications (Table 2), that compounds such as alkanes, naphthalene derivatives and benzene derivatives are found in char extracts, but not in bio-oils although they could be expected in this fraction [34,35]. A reason explaining their absence from bio-oils could be related to the high solubility of some of them with the aqueous fraction of the bio-oil that is not miscible with the CH_2Cl_2 solution. Water, acids, alcohols, aldehydes, ketones and sugar constituents are known to be water soluble [10]. As a result, in order to improve compound

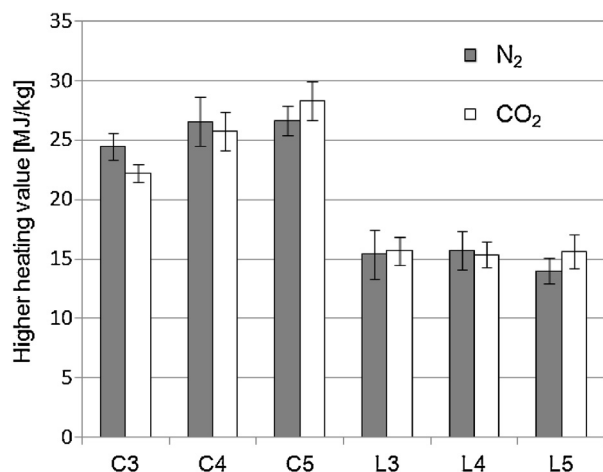


Fig. 4. Higher heating value of chars and bio-oils obtained at studied conditions. Error bars correspond to standard deviation.

identifications (for char extracts and bio-oils analyses), other types of solvents than dichloromethane with different polarity levels could be used, including methanol and water. The use of solvent with higher polarity could also corroborate the explanations about CO₂ reacting by carboxylation, which would have lead to compounds resilient to a dichloromethane solubilisation.

Among the grand total contents (Table 2), it can be observed that the total amount of compounds identified from the char extracts for each specific temperature shows a difference with respect to gas environment. At 300 °C, more compounds were identified under N₂ gas inflow environment than with CO₂, the inverse is however observed at 400 and 500 °C. This tendency among the grand total content of char extracts identified compounds is representative of some specific compounds categories total contents such as phenol derivatives and to alkanes and cyclopentanone derivatives at some extent (Table 2 and Fig. 2). This difference is mostly observed for char extracts compared to bio-oils where total contents with respect to gas environment per specific temperature are very similar. These results show that CO₂ environment has an effect on chemical products formed at low temperatures within the specific conditions of this study. Since CO₂ atmosphere was already observed to enhance carboxylic acid such as acetic acid [8,36] and that several observations made along this study could be explained by CO₂ reacting by carboxylation with the biomass constituents and pyrolysis products, the CO₂ environment could have reduced the decarboxylation reaction (prone at 300 °C) and even enhanced the reversed reaction (carboxylation) due to high CO₂ concentrations. In the case of the higher relative content obtained under CO₂ inflow environment at 400 and 500 °C, it is possible to note that several methyl and methoxy containing compounds appeared with higher relative content (Table 2; CO₂ vs. N₂ per specific pyrolysis temperature). Further quantified analyses of CO₂-pyrolysis products should be conducted on these compounds that weighted the most among the total contents in order to clarify the mechanisms that could have lead to the observed differences.

3.2. Calorific value

In addition to the chemical composition, the calorific value of the products was also determined. A significant lower calorific value was observed for chars produced at 300 °C in CO₂ vs. N₂ environments (22.2 vs. 24.5 MJ/kg respectively; $P < 0.05$) (Fig. 4). However, the char yields were lower at 300 °C-N₂ conditions vs. CO₂ (Table 1). For C3N conditions, char resulted in higher volatile loss and bio-oil yield compared to 300 °C-CO₂. As a result,

a higher fixed carbon content was obtained, which leads to a higher calorific value due mostly to carbon complete oxidation ($C + O_2 \rightarrow CO_2$) being more exothermic than volatiles oxidation containing other elements such as hydrogen, oxidizing through $2H + \frac{1}{2}O_2 \rightarrow H_2O$ (ΔH_f : -393.5 vs. -241.5 kJ/mol for CO₂ and H₂O(g) at 25 °C respectively). At 500 °C, the high fixed carbon with lower ash content can explain the higher heating value for C5C vs. C5N. As for the bio-oils heating value, no significant difference was observed with regards to the different temperature and vector gases. Bio-oils calorific value levels are consistent to the ones found in literature (~15 vs. 16–19 MJ/kg) [37], although, slightly lower calorific value for the bio-oils might be due to some compounds that were not possibly condensed and collected. This would be in agreement with Boateng et al.'s [10] bio-oil collecting system using condensers followed by an electrostatic precipitator, which lead to bio-oils heats of combustion of 16.0 and 21.7 MJ/kg (for condenser and electrostatic precipitator respectively).

4. Conclusions

The characterization of the solid and liquid pyrolysis products obtained from the medium pyrolysis of switchgrass in the targeted conditions showed that:

At 300 °C, char produced under CO₂ had higher extractible yields while its calorific value was significantly lower ($P < 0.05$) compared to N₂ environment (22.2 vs. 24.5 MJ/kg respectively).

At 400 °C, in char extracts, furfural was present only under N₂ conditions and found at significantly higher relative content in the bio-oils under N₂ vs. CO₂ environment. The lower furfural content under CO₂ conditions is consistent with the 1,4:3,6-dianhydro- α -D-glucopyranose concentrations in the char, which was found at higher concentrations under N₂ than CO₂ environment and is considered to be a precursor along furfural production.

Chars extracts were significantly lower at 500 °C, which was in accordance to lower volatile content found at these temperatures.

Among char extracts compounds identifications, lower grand total relative content were obtained at 300 °C in CO₂ gas inflow environment (vs. N₂), while the inverse was observed at 400 and 500 °C; a behavior consistent mostly with the phenol derivatives content, as well as with alkanes and cyclopentanone derivatives to some extent.

Char extracts had high phenol contents, which appeared to decline with respect to increasing temperatures while increasing in the bio-oils for the same conditions. Some phenol derivatives such as methoxy-phenol types mostly appeared at temperatures ranging from 300 to 400 °C, while other types of phenol derivatives did not show that trend.

In terms of PAHs, only naphthalene derivatives were found and only at 500 °C, where CO₂ appeared to enhance particularly the formation of 1,7-dimethyl-naphthalene and 2,7-dimethyl-naphthalene.

In char extracts, compounds containing carbonyl functional group, such as various ketones, were found only at 300 and 400 °C.

Introducing char extractable chemical compounds analysis along pyrolysis studies provided information for further value additions, some information that may also contribute to provide a better overview of pyrolysis conversion mechanisms; especially when presented in concert with bio-oil composition. In future research, the use of solvents with higher polarity levels to verify acidic compounds possibly resulting from carboxylation in CO₂ environment and aromatic solvents to add about PAH and other aromatic compounds concentrations could benefit eventual studies. Further quantification of the products of interest that demonstrated a difference with respect to gas environment would eventually be needed to corroborate the actual observations and for the value

additions of char with compounds that may or may not be desired at certain levels. In addition, since sources of CO₂ might come from flue gases, future works under typical flue gas mixture might also be of interest for industrial applications of the technology.

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